



# STUDIES ON THE SHRINKAGE PHENOMENON: XI. EFFECT OF PRETANNING TREATMENTS ON SHRINKAGE PROPERTIES OF COLLAGEN FIBRES

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A small amount of tension to which the fibres were subjected in the earlier technique<sup>1</sup> for determining linear changes associated with shrinkage influenced the shrinkage behaviour of collagen fibres. Tension reduces linear shrinkage (LS) and increases shrinkage temperature ( $T_s$ ) and linear recovery (LR). Hence a micro-shrinkage technique for measuring dimensional changes has been evolved. No difference in the micro-shrinkage values of raw, limed and delimed collagens was noticed. Only pickled samples showed a decrease in the  $T_s$  and LS and an increase in LR values. But in the case of shrinkage under the influence of 'a small tension', even pickled fibres behaved like raw, limed or delimed collagen fibres subjected to tension. This is attributed to the limited dilution of pickle in the micro-shrinkage method and infinite dilution in the other method. The shrinkage behaviour of limed collagen by micro method is not similar to that of limed skin, since liming lowers  $T_s$  as well as area shrinkage and increases area recovery.<sup>2</sup> This difference in behaviour is attributed to the lime in the void space of the three dimensional network structure of skin which renders the deliming influence of water less effective.

The shrinkage temperature, area shrinkage and wet and dry apparent volume shrinkage of hides and skins subjected to pretanning chemical treatments have been studied in detail.<sup>2-4</sup> Collagen being the basic fibrous protein constituent of hide or skin, it was considered desirable to study the shrinkage properties of collagen fibre bundles in order to have a better insight into the shrinkage phenomenon. In earlier work<sup>1</sup> on dimensional shrinkage of collagen fibres (Linear shrinkage and recovery) of variously tanned collagen fibres, purified acetone dehydrated KTT

was used as raw material. But acetone dehydration imparted a certain amount of stability of collagen;<sup>5-7</sup> it is well known that the acetone dehydrated skin or collagen does not wet back as a fresh material. Hence collagen fibres teased out from one year old albino rats and preserved in 0.5M salt solution at 4°C were used in the present experiment.

## Experimental

Rat tail tendon (RTT) was washed well with water, transferred to lime suspension and left overnight. Next

day, the fibres were washed well and delimed with 1% ammonium sulphate solution. They were then pickled with 0.5% sulphuric acid and 4% salt (w/v). The shrinkage values of the fibre bundles were measured at the end of each above treatment by the technique developed by Ramanathan *et al.*<sup>1</sup> The technique involves the suspension of the fibre in a water bath, the heating medium, with a small weight (0.5 g.) from the free end of the fibre to keep the fibre straight. After noting the initial length ( $l_1$ ) of the fibre suspended in the heating medium, the medium was heated at 2°C per minute, and the temperature at which the suspended fibre started shrinking was recorded. The final length ( $l_2$ ) of the shrunken fibre was noted on the completion of shrinkage i.e., when the temperature of

the bath is raised by about 5°C. The fibre was cooled in the same bath overnight for measuring the length after recovery. From these values, the linear shrinkage and linear recovery values were calculated using the following formulae,

$$LS (\%) = \frac{l_1 - l_2}{l_1} \times 100$$

$$LR (\%) = \frac{l_3 - l_2}{l_1 - l_2} \times 100$$

### Results and discussion

It may be seen from Table 1 that in the case of all pretanning treatments,  $T_s$ , LS and LR values vary considerably depending on the thickness of the col-

Table 1  
SHRINKAGE VALUES OF COLLAGEN FIBRES TESTED UNDER TENSION

Determination	Approximate thickness of the fibre bundles (mm.)	S. No.	Pretreatment given			
			Raw	Limed	Delimed	Pickled
Shrinkage temperature (°C)	Thin (0.2)	1	69	70	68	69
	Medium (0.8)	2	65	64	63	64
	Medium (1.0)	3	66	67	68	66
	Thick (1.6)	4	61	59	60	60
LS (%)	Thin (0.2)	1	60	61	62	60
	Medium (0.8)	2	68	68	65	68
	Medium (1.0)	3	64	66	65	68
	Thick (1.6)	4	70	69	72	71
LR (%)	Thin (0.2)	1	Fibre completely damaged during recovery			
	—	2				
	Medium (1.0)	3	60	58	57	62
	Thick (1.6)	4	42	46	48	48

LS — Linear shrinkage; LR — Linear recovery

lagen fibre bundles. The thinner the collagen fibre bundles used, the higher are the  $T_s$  and LR values and lower is the LS value; the linear recovery of the thinnest fibre bundles could not be measured as these fibres broke. However, a comparison of medium and thick bundles shows that the thinner bundles recovered in length to a greater extent. But, for a given thickness, the  $T_s$ , LS and LR values are almost constant for all the treatments. If the fibre bundles used for the experiment were very thin, they were ruptured during the recovery. It was also noticed that the influence of the small suspended weight (0.5 g.) on dimensional shrinkage values (LS & LR) of collagen is less if acetone dehydrated fibres are used for the experiment instead of salt preserved ones. These observations indicate that the tension, however small, does influence the shrinkage characteristics. This is so because the load per unit area (arising out of the weight attached to the fibre bundle in the shrinkage experiment) helps the recovery but opposes the shrinkage.

The present finding that there is no appreciable difference in the shrinkage values of collagen fibres subjected to pretanning treatments, and the previous finding<sup>2</sup> that, in the case of hide or skin subjected to similar treatments, the shrinkage temperature and area shrinkage of limed and pickled samples were appreciably lowered and area recovery was enhanced, demonstrate the difference in the behaviour of skin and collagen fibres towards shrinkage. Unlike hide or skin which is a well interwoven three dimensional network of collagen fibres, RTT can be considered

as a parallel array of collagen fibres. This basic difference is responsible for the very quick effect of any treatment on RTT and rather slow effect on hide or skin. The difference in shrinkage behaviour of limed and delimed skin observed earlier<sup>2</sup> is due to the slow deliming action of water on limed skin. Considerable swelling of pickled skin during shrinkage or recovery in water is due to the slow depickling action of water, resulting in limited dilution of pickle. In the absence of a network structure in the fibres, any treatment is effective in a very short time. This is supported by the visual observation that when pickled collagen was placed in water (the heating medium), immediate swelling caused by the limited dilution of the pickle soon subsided due to the infinite dilution of pickle.

As further evidence for the influence of tension on shrinkage values and for determining the dimensional shrinkage values of collagen fibres free from the influence of tension, a micro-shrinkage method of finding dimensional shrinkage, which gives values for the fibres in the free state, was evolved and is described below.

[*Method of free shrinkage:* This method is an improvement over the technique developed by Nutting and Borasky.<sup>8,9</sup> A collagen fibre bundle of 0.2 cm. length subjected to a particular pretanning treatment was placed on a cavity slide containing a few drops of water and covered with a micro cover slip. The slide was placed on a micro hot plate which, in turn, was placed over the mechanical stage of a micro projector

and a 10 $\times$  objective was used. The fibre was focussed and a magnified image was projected on the screen. The contours of the image of the sample before and after shrinkage, and after recovery were traced. From the average values of magnified lengths, LS and LR were calculated. The  $T_s$  of the sample, as indicated by a thermometer inserted in the hot stage, was noted].

For comparing the values obtained by the method under tension and the method described above, a uniform collagen fibre bundle was cut into two parts, i.e., 3 cm. and 0.2 cm. long. The former method was used for the longer part and the latter method for the shorter. For each pretanning treatment, several fibre bundles were tested.

For assessing the effect of each pretanning treatment on the  $T_s$  and dimensional shrinkage by the micro-shrinkage method, a uniform collagen fibre bundle was soaked. A part of the bundle from one end was cut and used for the determination of  $T_s$  and dimensional shrinkage values. The remainder of the bundle was limed and a further part cut out next to the part already taken away. This procedure was followed for all the treatments and the experiment repeated for several bundles.

The gross variation in shrinkage values with the thickness of the bundles using the method under tension is not there if the measurements are carried out in the free states; also  $T_s$ , LS and LR values of samples in the raw, limed and delim-

Table 2

COMPARISON OF SHRINKAGE VALUES OF COLLAGEN FIBRES TESTED UNDER TENSION AND IN THE FREE STATE

Determination	S. No.	Pretreatment given			
		Raw	Limed	Delimed	Pickled
$T_s$ ( $^{\circ}$ C)	1	69(55)	67(56)	68(57)	69(37)
	2	64(56)	64(57)	66(55)	64(35)
	3	66(55)	68(56)	67(56)	65(36)
	4	62(56)	62(55)	60(55)	59(37)
LS (%)	1	61(73)	62(76)	56(76)	55(39)
	2	67(72)	65(72)	65(76)	65(38)
	3	64(76)	66(76)	62(75)	64(41)
	4	70(76)	(70)	70(74)	67(42)
LR (%)	1	Fibre broken in the case of testing under tension			
		(10)	(10)	(9)	(46)
	2	55(10)	48(14)	56(13)	61(50)
	3	60(10)	62(14)	70(13)	61(50)
	4	42(10)	46(13)	48(9)	48(40)

Shrinkage values in the free state are given in the parenthesis.  
Thickness of the fibre bundle is as in Table 1.

ed stages are less (Table 2). In the case of pickled samples shrunk in the free state, the decrease in  $T_s$  is greater compared to the samples tested under tension, and LS is also lowered. Still LR value of the sample is quite appreciable. Comparison of shrinkage values in the free state of adjacent pieces of collagen fibres subjected to pretanning treatment (Table 3) shows that there is no appreciable difference in  $T_s$ , LS and LR values of raw, limed and delimed samples. Only pickled samples showed a considerable decrease in  $T_s$  and LS and an increase in LR.

Table 3  
SHRINKAGE VALUES IN THE FREE STATE\*

	Raw	Limed	Delimed	Pickled
$T_s$ (°C)	56	54	55	36
LS (%)	74	75	75	41
LR (%)	12	11	10	49

\* Average of six values

The higher  $T_s$  of samples shrunk under tension compared with the corresponding free shrinkage values of raw, limed and delimed collagen confirms the view that the small suspended weight, however small, does influence the shrinkage characteristics of collagen. The absence of a difference in shrinkage behaviour of raw, limed and delimed collagen shrunk in the free state, in contrast to the different shrinkage behaviour of skins subjected to pretanning treatment<sup>2</sup> i.e., lower  $T_s$  and area shrinkage values and higher recovery values, is perhaps due to quick nullification of swelling effects of lime when limed collagen fibres were transferred

from saturated lime into water; this in turn has made the limed collagen fibres behave like delimed collagen samples. In the case of micro-shrinkage of pickled samples, the lower  $T_s$  and LS values in contrast to those tested under tension are due to the limited dilution caused by only two drops of water used as the testing medium on the cavity slide and the absence of influence of tension. The reduction in LS value on account of swelling is also perhaps responsible for the better recovery figure of pickled sample. It is thus confirmed that no appreciable difference in  $T_s$ , LS and LR values of raw and pickled collagen bundles tested under tension is due to the depickling effect caused by the infinite dilution of the pickle by the water, the heating medium.

The small amount of recovery observed in the case of shrinkage under free state of raw and delimed collagen may only be due to the uptake of water since only crosslinked collagen (tanned) exhibits good recovery.<sup>10</sup>

RTT did not withstand the fairly long liming treatment given for processing of hides and skins and was gelatinised. Hence RTT was treated with saturated lime overnight and the shrinkage behaviour of skin and collagen was compared though the processing was not identical. Thus the comparison does indicate a gross difference in the shrinkage behaviour of skin and collagen fibres.

It is concluded that the small amount of tension appreciably influences the shrinkage characteristics of collagen and a micro-shrinkage method for measuring

dimensional changes caused by shrinkage is recommended.

There is no difference in  $T_s$ , LS and LR values of raw, limed and delimed collagen. This is in contrast to the shrinkage characteristics of skin where  $T_s$  and area shrinkage were lowered and recovery was enhanced on liming and again the behaviour reversed on deliming. However, at the pickling stage, the shrinkage behaviour of skin and collagen is similar. The shrinkage temperature and linear shrinkage of the pickled collagen are decreased and linear recovery is greatly increased.

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